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(54) CARBON NANOFIBER COMPOSITE AND ITS MANUFACTURING METHOD

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a carbon nanofiber composite in which carbon nanofibers are grown in high density on a surface of a substrate.
SOLUTION: A substrate 1 that is a solid solution phase consisting of a transition metal oxide and a nonreducible metal oxide is heated up in a methane gas and then the transition metal oxide is reduced and the transition metal is formed on the surface of the substrate and then the carbon nanofibers 2 are precipitated from this transition metal.

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CLAIMS

[Claim(s)]

[Claim 1] Carbon nano fiber complex characterized by consisting of a base containing a solid-solution phase with the oxide of transition metals, and a difficulty reducibility metallic oxide, and a carbon nano fiber grown up from said transition metals which deposited on this base.

[Claim 2] The manufacture approach of the carbon nano fiber complex characterized by growing up a carbon nano fiber from said transition metals which heated the base containing a solid-solution phase with the oxide of transition metals, and a difficulty reducibility metallic oxide under the reducing atmosphere, deposited said transition metals on said base front face, and heated and deposited in the gas which uses said base as a carbon configuration element.

[Claim 3] The manufacture approach of the carbon nano fiber complex characterized by growing up a carbon nano fiber from said these depositing transition metals while heating the base containing a solid-solution phase with the oxide of transition metals, and a difficulty reducibility metallic oxide in the gas which uses carbon as a configuration element and forming said transition metals in said base front face.

[Claim 4] Said difficulty reducibility metallic oxide is carbon nano fiber complex according to claim 1 which is the oxide of at least one sort of metals chosen from Cu, Zn, Sn, Cd, Pb, Hg, and Ag, and is

characterized by being 0.1 - 50atm% to said transition metals.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to carbon nano fiber complex and its manufacture approach.

[0002]

[Description of the Prior Art] A carbon nano fiber is called a carbon nanotube or a graphite nano fiber, it is fiber of the carbon which has the diameter of dozens of nm or less, and the application as the electrode material of a cell, an emitter ingredient for a display, etc. is expected.

[0003] since the carbon nano fiber obtain by compound this ingredient by contact carbon content gas , such as methane , to the catalyst particle which generally consist of transition metals , and decompose carbon content gas into it from a gaseous phase , and do in this way had the random direction where each fiber grow , it be difficult to use it as the aggregate which carried out densification of the carbon nano fiber .

[0004] On the other hand, a fuel cell has little emission of a carbon dioxide, and it is greatly observed as few generation-of-electrical-energy techniques of an environmental load in recent years.

[0005] In the cathode of this fuel cell, the reaction which the oxygen supplied from the outside and the hydrogen ion supplied from an electrolyte are contacted for a catalyst, and generates water generates an electron hole, and this electron hole is supplied to a lead terminal (an electron is supplied to a catalyst from a lead terminal). Therefore, in order to supply an electron to a catalyst, the electrode material is used for the Plastic solid which fabricated the carbon particle which usually supported the catalyst using the binder etc.

[0006] However, in the electrode which fabricated the carbon particle using the binder etc., electronic loss arises between carbon particles.

[0007] Since the conventional carbon nano fiber is growing up one carbon nano fiber from each transition-metals particles, such as nickel, homogeneity and high density must be distributed on a substrate front face, and it must make it support the transition metals of a uniform particle size, although it is possible to reduce electronic loss using

the carbon nano fiber which can lengthen fiber length to the particle size of a carbon particle. Consequently, since a precise activity is needed, the problem that the productivity becomes very low arises.

[0008]

[Problem(s) to be Solved by the Invention] As mentioned above, since the conventional carbon nano fiber was grown up from the particle which consists of transition metals, such as nickel, it was difficult to carry out densification.

[0009] In view of such a problem, it succeeds in this invention, and it aims at offering the carbon nano fiber complex which grew up two or more carbon nano fibers into the base front face directly, and its manufacture approach.

[0010]

[Means for Solving the Problem] The carbon nano fiber complex of this invention is carbon nano fiber complex characterized by growing up from the base containing a solid-solution phase with the oxide of transition metals, and a difficulty reducibility metallic oxide, and said transition metals which deposited on this base, and consisting of a *** carbon nano fiber.

[0011] Said difficulty reducibility metallic oxide is an oxide of at least one sort of metals chosen from Cu, Zn, Sn, Cd, Pb, Hg, and Ag, and it is desirable to carry out at 0.1 - 50atm% to said transition metals.

[0012] The manufacture approach of the carbon nano fiber complex of this invention is characterized by having growing up a carbon nano fiber from said transition metals which heated the base containing a solid-solution phase with the oxide of transition metals, and a difficulty reducibility metallic oxide under the reducing atmosphere, deposited transition metals on said base front face, and heated and deposited in the gas which uses said base as a carbon configuration element.

[0013] Moreover, the manufacture approach of the carbon nano fiber complex of this invention is characterized by growing up a carbon nano fiber from these depositing transition metals while it heats the base containing a solid-solution phase with the oxide of transition metals, and a difficulty reducibility metallic oxide in the gas which uses carbon as a configuration element and forms transition metals in said base front face.

[0014]

[Embodiment of the Invention] Hereafter, explanation of this invention is given using a drawing.

[0015] Drawing 1 is the conceptual diagram of the carbon nano fiber complex concerning this invention.

[0016] The base 1 is formed by the solid solution of the oxide of transition metals, and a difficulty reducibility metallic oxide, the carbon nano fiber 2 is growing from the field where the transition-metals element of this base 1 front face exists, and, as for this carbon nano fiber, two or more are formed all over the base 1.

[0017] As it will not be restricted especially if the solid-solution phase of the oxide of transition metals and a difficulty reducibility metallic oxide is contained, for example, shown in drawing 1, the substrate formed with the solid-solution phase may be used for a base 1 as a base as it is, and the base with which said solid-solution phase was formed in the substrate front face which consists of insulating ingredients, such as conductive ingredients, such as a metal or carbon, and ceramics, may be used for it.

[0018] That what is necessary is just to use oxides, such as Fe, CO, or nickel, the oxide of transition metals returns these oxides and forms transition metals into a solid-solution phase. A carbon nano fiber grows by making these transition metals into a catalyst.

[0019] Moreover, metals, such as Cu, Zn, Sn, Cd, Pb, Hg, or Ag, or the oxide of these alloy contents can be made to contain in the solid solution. If such a metal is made to contain in the solid solution, transition metals and these metals will carry out an alloy, and a carbon nano fiber will grow from this alloy. As a result, the function as a catalyst increases, and it becomes possible to grow up a homogeneous carbon nano fiber efficiently.

[0020] For example, using the solid-solution phase of the ternary system which consists of the oxide of transition metals, a difficulty reducibility metallic oxide, and an oxide of an alloy content, the solid-solution phase of this ternary system can be returned, the alloy which consists of transition metals and an alloy content can be deposited, and a carbon nano fiber can be grown up from this alloy.

[0021] Therefore, in case these alloy contents are used, a difficulty reducibility metallic oxide is wanted to use an ingredient with reducibility lower than the oxide of an alloy content. In addition, as for the ratio which mixes elements, such as Cu, Zn, Sn, Cd, Pb, Hg, or Ag, it is desirable to consider as 0.1 – 50atm% to transition metals.

[0022] It is desirable to use the metallic oxide which a difficulty reducibility metallic oxide points out the oxide of a metal at least with reducibility lower than the oxide of transition metals, and is not especially returned to a metal under 15 degrees C – 700 degrees C hydrogen or plasma conditions. If the metallic oxide returned to a metal under 15 degrees C – 700 degrees C hydrogen or plasma conditions is used,

even a difficulty reducibility metallic oxide will be returned at the time of reduction of transition metals, there is a possibility that the alloy of transition metals and a difficulty reducibility metal may deposit, and, as a result, the function as a catalyst of transition metals will be reduced.

[0023] As such a difficulty reducibility metal, aluminum, Mg, Si, Zr, Ti, Hf, calcium, or Ce can be mentioned, for example.

[0024] Moreover, as for a difficulty reducibility metallic oxide, it is desirable to choose the ingredient which all dissolves between the oxides of transition metals, and the ratio of the oxide of transition metals and a difficulty reducibility metallic oxide can be set as any value by choosing such an ingredient. As combination of all oxides of the dissolving transition metals and difficulty reducibility metallic oxides, the combination of NiO-MgO, FeO-MgO, or CoO-MgO is mentioned, for example. Moreover, it may not be restricted to the combination which all dissolves, but what combined the ingredient which dissolves and suits only by the ratio of the predetermined range is sufficient as the ternary system of Zr, nickel, and O, the ternary system of Ti, nickel, and O, or the ternary system of Ce, nickel, and O.

[0025] Moreover, as for the ratio of the oxide of the transition metals in the solid solution layer which consists of a difficulty reducibility metallic oxide and an oxide of transition metals, it is desirable to consider as a 30 - 70wt% ingredient.

[0026] If the ratio of the oxide of transition metals is not filled to 30wt(s)%, it will become difficult to return the oxide of transition metals. Consequently, there is a possibility that the catalyst (transition metals) for growing up a carbon nano fiber may no longer be generated. Moreover, when 70wt% was exceeded and a solid solution layer is returned, it becomes difficult to control the particle size of the transition metals which deposit. That is, there is a possibility that the particle size of the transition metals which deposit as a catalyst may become large, consequently the diameter of the carbon nano fiber which grows up to be a catalyst front face may become large.

[0027] The carbon nanotube concerning this invention is the carbon material of graphite structure, and has some which carried out the configuration which carried out the fiber configuration with a diameter of 1 micrometer or less, for example, carried out the laminating of the c-th page of graphite in the fiber length direction, and the tube configuration which uses the c-th page of graphite as a side attachment wall.

[0028] Next, the manufacture approach of the carbon nano fiber of this

invention is explained.

[0029] First, the manufacture approach of the base mentioned above is explained.

[0030] After preparing difficulty reducibility metallic-oxide powder and the oxide powder of transition metals and mixing by the desired ratio, the solid solution is producible by heating to an elevated temperature 1000 degrees C or more, and carrying out the pyrogenetic reaction of both the powder.

[0031] As for the powder used for this raw material, it is desirable to use impalpable powder with a mean particle diameter of about 1-100 micrometers. If particle size is smaller than 1 micrometer, workability will worsen, and if particle size is larger than 100 micrometers, the uniform solid solution will not be obtained, but only the field where the concentration of the oxide of transition metals is high will be returned alternatively, and there is a possibility that a desired carbon nano fiber may no longer be obtained.

[0032] This solid solution may be used as a base as it is, a glass substrate etc. may use this solid solution as a raw material on a desired substrate front face, and the layer which consists of the solid solution by the spatter, PVD, etc. may be formed. Furthermore, the thin film layer which becomes a base front face from the solid solution with wet synthesis methods, such as a sol gel process, can be formed.

[0033] As for the thickness of the layer which consists of the solid solution, it is desirable to be referred to as 0.01 micrometers or more and 10 micrometers. There is a possibility that the transition-metals particle of sufficient particle size to function as a catalyst may not deposit if thickness is smaller than 0.01 micrometers, if thickness is larger than 10 micrometers, adhesion with a substrate will fall or formation of the layer which consists of the solid solution will become difficult.

[0034] Moreover, electric connectability with a substrate is controllable by making thin thickness of the layer which consists of the solid solution. For example, when connecting to a conductive substrate front face the carbon nano fiber electrically connected with this conductive substrate, a carbon nano fiber and a conductive substrate can be electrically connected by setting to 0.01 micrometers or more and 1 micrometer or less thickness of the layer which consists of the solid solution. That is, the transition metals which constitute a part of layer which consists of the solid solution are returned, and since a conductive substrate is connected with a carbon nano fiber through transition metals with this conductivity, electric connection can be

given between a carbon nano fiber and a conductive substrate, so that it may mention later.

[0035] Moreover, as the solid solution, if a conductor or a semiconductor is used, conductivity can be given between a carbon nano fiber and a substrate irrespective of the thickness of the solid solution.

[0036] What is necessary is to use the insulating solid solution, to set to 0.01 micrometers or more and 10 micrometers or less thickness of the layer which consists of the solid solution and just to form the substrate to be used with an insulating ingredient to produce the insulating substrate which has a carbon nano fiber on a front face naturally.

[0037] Next, how to grow up a carbon nano fiber into this base front face is explained more to a detail.

[0038] For example, the substrate (namely, base containing the solid solution layer of the oxide of transition metals and a difficulty reducibility metallic oxide) which has the solid-solution layer mentioned above is heated under reducing atmosphere, the oxide component of the transition metals in a solid solution layer is returned, and transition metals are deposited.

[0039] Furthermore, the substrate which has a solid-solution layer can be heated in the hydrocarbon gas ambient atmosphere which is material gas of a carbon nano fiber, hydrocarbon gas can be decomposed by the ability making these depositing transition metals into a catalyst, and fibrous carbon can be deposited on these depositing transition metals. That is, a carbon nano fiber can be grown up into a transition-metals front face.

[0040] As reducing gas for returning the oxide component of transition metals, hydrocarbon gas can be used and a deposit of transition metals and the carbon on this front face of transition metals can be deposited to coincidence.

[0041] When transition metals are deposited with another reducing gas, and carbon is deposited after completing reduction, there is a possibility that the particle size of depositing transition metals may become large, and the diameter of the carbon nano fiber which grows up to be a transition-metals front face as a result may become large.

[0042] Therefore, it is desirable to grow up a carbon nano fiber at the same time it returns transition metals by heating in a hydrocarbon the base which has a solid solution layer.

[0043] Thus, since the carbon nano fiber complex obtained is growing up the direct carbon nano fiber from the transition metals which constitute some bases, compared with the case where the carbon nano fiber produced

separately is made to adhere to a substrate, the junction force of a carbon nano fiber over a base will become big.

[0044] Moreover, while a carbon nano fiber crowds, in order to grow up to be coincidence, orientation of each carbon nano fibers is perpendicularly carried out to a base side.

[0045] As material gas used for growth of a carbon nano fiber, it is not restricted to methane but hydrocarbon gas, such as ethylene gas and acetylene gas, can also be used. Moreover, if it is gas of carbon content which can return the oxide component of transition metals, contacts transition metals, is decomposed, and deposits carbon as material gas even if it is not hydrocarbon gas, it can be used, for example, said base can be heated in this mixed gas using the mixed gas of carbon dioxide gas, such as a carbon monoxide or a carbon dioxide, and hydrogen gas, a deposit of transition metals and the carbon on this front face of transition metals can be deposited, and a carbon nano fiber can also be grown up. Moreover, it may arrange in the container which had the base concerning this invention decompressed, and material gas may be introduced into this decompressed container.

[0046] Moreover, when using hydrocarbon gas as material gas, it can also use as mixed gas with inert gas, such as hydrogen, and Ar, helium. The ethylene gas of using it as such mixed gas etc. is especially desirable, in case many carbon components are contained and use unstable hydrocarbon gas thermally. That is, since the carbonaceous deposit rate of unstable hydrocarbon gas is quick, it is easy to produce dispersion to the size of a carbon nano fiber which grows up to be a transition-metals front face, die length, etc., and, occasionally carbon may not grow in the shape of a fiber.

[0047] For example, the base concerning this invention is arranged in a 350 degrees C - 1000 degrees C reaction container, a material gas partial pressure is introduced at 10 - 100%, and it becomes possible to grow up a carbon nano fiber on a base by making it react for 10 minutes to about 10 hours.

[0048] There are few material gas partial pressures with whenever [stoving temperature / lower than 350 degrees C] than 10%, or if reaction time is shorter than 10 minutes, transition metals do not deposit, or a transition-metals front face does not deposit in carbon, but there is a possibility that a carbon nano fiber may not grow up to be a base front face. Moreover, there is a possibility that the diameter of the carbon which deposits when reaction temperature is higher than 800 degrees C may become large.

[0049] Since it becomes possible to form the countless minute field

which consists of returned transition metals by arranging the base containing a solid-solution phase with the oxide of transition metals, and a difficulty reducibility metallic oxide under reducing atmosphere according to this invention as explained in full detail above, it enables this base front face to grow up a carbon nano fiber into high density.

[0050]

[Example] 0.1 micrometers of NiO-MgO solid-solution layers were formed on the substrate front face on which the production NiO and MgO of an example 1 carbon nano fiber consists of porosity carbon using the solid-solution target of 2:1 by the mole ratio, and the base which has a solid-solution phase was produced.

[0051] Subsequently, the obtained base was contained in the electric heating furnace, atmospheric pressure methane was introduced by the flow rate of 100 cc/min, and heat treatment was performed at 800 degrees C for 1 hour.

[0052] When the base was taken out from the electric heating furnace after heat treatment and the front face was observed, it was checked that the carbon nano fiber complex which the countless carbon nano fiber whose die length is about 1.5 micrometers deposited [complex] perpendicularly to the base side for the diameter of about 30nm, and grew up the carbon nano fiber into the base front face in average size is obtained.

[0053] making it dry, after settling Pt by applying to the carbon nano fiber front face of the application profit **** carbon nano fiber complex to a fuel cell into a chlorination Pt acid water solution, and a sodium hydrogencarbonate being further dropped at a chlorination Pt acid water solution, and making both react -- a carbon nano fur bar front face -- Pt particle as a catalyst for fuel cells -- 10wt(s)% -- the cathode made to support was produced.

[0054] As an anode, the electrode which was applied and solidified and which is usually used was prepared for the carbon cross front face with the catalyst binder which made the carbon particle front face support a Pt-Ru particle.

[0055] The foil-like electrolyte membrane (Du Pont make: product name Nafion) was inserted into inter-electrode [this / of two sheets], and the fuel cell cel was produced.

[0056] When delivery was conducted to the anode of this fuel cell cel and delivery and a generation-of-electrical-energy experiment were conducted [the two mol% methanol water-solution fuel] for air on the cathode, the generation of electrical energy of 100 mW/cm² has been

checked.

[0057] Except for having used the cathode obtained like the anode used in the example 1 except for having used Pt particle instead of the example of comparison 1 Pt-Ru particle, the fuel cell cel was produced like the example 1.

[0058] When the generation-of-electrical-energy trial of this fuel cell was performed like the example 1, the generation of electrical energy of 20 mW/cm² has been checked.

[0059] Except for having used the solid-solution target of the presentation shown in two to example 6 table 1, the base which has a solid-solution phase like an example 1 was produced.

[0060] Furthermore, heat treatment shown in Table 1 to this base was performed, and the carbon nanotube was grown up into the base front face.

[0061] In addition, the conditions of an example 1 are also written together in Table 1.

[Table 1]

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Thus, when the obtained carbon nano fiber complex was observed, it has checked that the countless carbon nano fiber whose die length is about 1.5 micrometers was growing for the diameter of about 30nm like the example 1.

[0062] Furthermore, when the fuel cell was produced like the example 1 and the generation-of-electrical-energy output was measured using these carbon nano fiber complex, in an example 2 thru/or 6, they were 60 mW/cm², 65 mW/cm², 85 mW/cm², 80 mW/cm², and 75 mW/cm², respectively.

[0063] Thus, if the carbon nano fiber complex of this invention is used for a fuel cell, it will become possible to carry out a high increase in power of the fuel cell.

[0064] In addition, in this example, although the solid-solution phase was formed in the porosity support substrate front face and the carbon nano fiber was grown up, a solid-solution phase may be formed in a metal substrate front face.

[0065] Usually, since the acid electrolytic solution is used for a fuel

cell, if a metal substrate is used, a substrate will corrode. However, since it is covered with the carbon nano fiber complex of this invention by the solid solution which generally consists of a stable ceramic chemically, it is possible to reduce the corrosion of the metal substrate at the time of using it in an acid ambient atmosphere.

[0066]

[Effect of the Invention] As mentioned above, according to this invention, it is possible to obtain the carbon nano fiber complex which grew up the carbon nano fiber into the substrate front face at high density.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view of the carbon nano fiber of this invention.

[Description of Notations]

1 -- Base

2 -- Carbon nano fiber
